ASSESSING HERBICIDE MOVEMENT USING SOIL SAMPLES VERSUS PERCOLATE SAMPLES

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ABSTRACT. *Soil core samples are often used to assess herbicide movement through soil or to evaluate contaminant transport models. When macropore flow occurs, the suitability of soil cores for these purposes is questionable. Our objectives were to evaluate the effectiveness of soil samples from a macroporous soil as the sole means to assess herbicide movement in percolate and to assess a contaminant transport model. To accomplish this, atrazine and alachlor were surface-applied to 30 × 30 × 30 cm blocks of undisturbed, no-till silt loam soil at three moisture levels (dry, intermediate, wet) then subjected to a 0.5-h, 30 mm simulated rain. Percolate was collected from the base of the blocks and the soil was sampled by slicing the blocks into eight, 3.75 cm-thick, horizontal slabs. The contaminant transport model GLEAMS was used to predict herbicide concentration in the percolate and soil. The model was calibrated to equate the observed and predict percolate volume by adjusting the initial water content. Further model calibration was performed for two modeling scenarios: (1) to equate the observed and predicted herbicide concentration in the bottommost soil layer (26.25-30 cm) or (2) to equate the observed and predicted herbicide concentration in the surface soil layer (0-3.75 cm). No correlation was observed between herbicide concentration in soil and herbicide concentration in percolate. GLEAMS was calibrated to accurately predict percolate volumes and herbicide concentration in soil, but herbicide concentration in percolate was substantially under-predicted in most instances by a factor of 6 to 123. Our results indicate that the soil sampling strategy used in this study was a poor indicator of subsurface herbicide movement in percolate and ineffective as the sole means to assess contaminant transport models in soils subject to macropore flow.*

Keywords. *Atrazine, Alachlor, Pesticides, Leaching, Experimental design, Transport modeling, GLEAMS.*

For many soils, vertical water movement is through only a small portion of the total porosity due to macropore flow (root channels, earthworm holes, cracks, etc.) and macropore flow may be widespread (Rawls et al., 1996). Field and laboratory studies suggest that soil samples may not be effective to study herbicide movement through soils subject to macropore flow (e.g., Essington et al., 1995; Shipitalo et al., 1990; Flury, 1996). Nevertheless, soil cores are sometimes the sole method used to assess herbicide movement (e.g., McDonald et al., 1999; Vicari et al., 1994; Troiano et al., 1993; Pantone et al., 1992). Moreover, soil samples are sometimes the only method used to test a model's ability (e.g., PRZM, GLEAMS, LEACHMP) to predict pesticide movement (e.g., Khakural et al., 1995; Zacharias and Heatwole, 1994). If soil samples are unrepresentative of herbicide movement in percolate under these conditions, it may be wise to consider using other, possibly more representative, methods to assess pesticide movement such as pan lysimeters, monolith lysimeters, subsurface drains, and monitoring wells.

Pesticide contamination of groundwater is a potential health and environmental issue (e.g., Wade et al., 1998). For most herbicides, soils, and management scenarios, the great majority of the herbicide will remain in the near-surface soil but a small portion can be transported in percolate and potentially transported to groundwater. As Steenhuis et al. (1990) indicated, if even 0.1% of a 2-kg/ha application of a chemical reaches the groundwater, concentrations in excess of 1 μg/L would result (note that the lifetime Health Advisory Level-Maximum Contaminant Level, HAL-MCL, for atrazine is 3 μg/L and the MCL for alachlor is 2 μg/L). Also, Bouwer (1990) indicated that predictive modeling of pesticide movement will always be difficult because of the complexities of the processes and the fact that often only a small amount of the pesticide applied will actually move to underlying groundwater.

Therefore, our objectives were to evaluate, under controlled laboratory conditions where sample variability is reduced compared to field conditions, the effectiveness of soil samples from a macroporous soil as the sole means to (1) assess herbicide movement in percolate, and (2) assess a contaminant transport model (GLEAMS).

Article was submitted for publication in May 1999; reviewed and approved for publication by the Soil & Water Division of ASAE in February 2000.

Contribution from the USDA-Agricultural Research Service, North Appalachian Experimental Watershed (NAEW), Coshocton, Ohio.

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Materials and Methods

The most critical percolate event in soils subject to macropore flow is often the first rainfall after herbicide application because this is when herbicide concentrations in the percolate are frequently highest (Malone et al., 1996; Kladivko et al., 1991). Therefore, we reevaluated percolate concentration data in the first rainfall after herbicide application in a macroporous soil previously reported in Shipitalo and Edwards (1996) and combined this with heretofore unreported soil concentration data. For the purposes of this article, percolate is defined as the water that drains freely from the bottom of a 30-cm-deep soil block.

Soil Blocks

Eleven 30 × 30 × 30 cm blocks of undisturbed soil (Glenford silt loam: fine-silty, mixed, *mesic Aquic Hapludalf*) were collected from a field that had been no-till planted with corn (*Zea mays* L.) for 10 years. Details of the soil block collection procedure and the block experiment can be found in Shipitalo and Edwards (1996). Three blocks were randomly assigned to each of three antecedent soil water levels (dry, ≈17% mL/mL; intermediate, ≈27%; and wet ≈33%). The intermediate and wet moisture levels, respectively, were attained by sprinkling either 30 mm or 60 mm of distilled water on the blocks at a rate of 15 mm/h; the dry blocks did not have additional water applied. After water was applied the blocks were covered and allowed to equilibrate for 7 d. Atrazine and alachlor were dripped onto the blocks in 5 mL of water at rates equivalent to 2.25 and 4.5 kg a.i./ha, respectively, followed 1 h later by a 0.5-h, 30-mm simulated rainfall. Percolate was collected at atmospheric pressure from each cell of a 64-square grid lysimeter (3.75 × 3.75 cm cells) in approximately 10 mL increments. Thirty minutes after simulated rainfall ceased, the blocks were sliced into eight horizontal slabs (≈3.75 cm) that were subsequently weighed, mixed, and sampled for herbicide and gravimetric moisture analysis. The thickness of each slab of each block was estimated using the dry soil weight of each slab, average bulk density of each block (≈1.54 g/cm^3), and area of each block (900 cm^2); these values were also input into GLEAMS. Background herbicide concentrations were determined from two control blocks that did not receive herbicide applications.

Statistical Analysis

The mixed model procedure of SAS (ver. 6.12) was used to analyze herbicide concentrations separately for each of the bottom three layers of soil (≈18.75 to 30 cm) and the percolate. The mixed model was used because partitioning the residual variance between treatments and the control was necessary due to variance heterogeneity. Dunnett's procedure was used to separate means. The alternative hypothesis was that the treatment mean was significantly greater than the control mean. Because alachlor concentration in the control soil and alachlor and atrazine concentrations in the control percolate were below detection limits, a negligible value (0.001 μg/g for soil samples; 0.001 μg/mL for percolate) was added to one of the replicates to permit the mixed model to converge.

Table 1. Selected GLEAMS input parameters

Parameter	Block Condition: Dry	Inter.	Wet
Soil depth (cm)			
Layer 1	4.05	4.42	3.54
Layer 2	15.02	15.23	14.97
Layer 3	26.65	26.35	26.41
Layer 4	30.0	30.0	30.0
Initial fraction of plant available water (BST)*	0.60	0.60	0.75
Porosity (POR) (cm/cm)†	0.42	0.42	0.42
Field capacity (FC) (cm/cm)‡	0.33	0.33	0.33
Wilting point (BR15) (cm/cm)‡	0.12	0.12	0.12
Clay (%)‡	20	20	20
Silt (%)‡	60	60	60
% organic matter†			
Layer 1	4.5	4.5	4.5
Layer 2	4.5	4.5	4.5
Layer 3	2.09	2.09	2.09
Layer 4	1.55	1.55	1.55
Atrazine K_{oc} (mL/g)*			
Surface layer calibration	44	22	42
Bottom layer calibration	20	12	14
Alachlor K_{oc} (mL/g)*			
Surface layer calibration	80	44	80
Bottom layer calibration	35	39	27

* Calibrated.
† Measured.
‡ Default (provided by model given soil type).

Modeling

The contaminant transport model GLEAMS (ver. 2.10), described in Knisel et al. (1993) and Leonard et al. (1987), was used to predict herbicide concentration in the percolate. Default, measured or calibrated input parameters were used as indicated in table 1. Each soil moisture condition was modeled with four soil layers, determined as the average depth increment from the three replications. Predicted percolate volume was calibrated to closely approximate the average observed volume (4.8 mm for the intermediate and dry blocks; 14.2 mm for the wet blocks) by adjusting the fraction of available water using trial and error. The predicted herbicide concentration in the surface soil layer (≈0 to 3.75 cm) or bottom soil layer (≈26.25 to 30 cm) was calibrated to closely approximate the observed soil herbicide concentration after percolation had ceased by adjusting the atrazine and alachlor partition coefficients (K_{oc}) using trial and error. Kumar et al. (1998) also used the technique of adjusting the K_{oc} values to calibrate a transport model. The model parameter input scheme was somewhat simplistic therefore, sensitivity analysis was used to investigate the effect of field capacity, porosity and organic matter on GLEAMS predicted percolate concentration compared to soil concentration.

Results and Discussion

Soil Blocks

Herbicide concentration in the percolate were greatest for the dry soil and lowest for wet soil (table 2), suggesting more macropore flow in the dry soil (Shipitalo and Edwards, 1996). The herbicide concentrations for the bottom three soil layers of the dry soil, however, were not significantly greater than the control. In the wet blocks, three of six comparisons indicated that herbicide concentrations in soil were significantly greater than the control. Therefore, soil analysis indicated no significant

Table 2. Measured herbicide concentrations in the bottom three soil layers and in the percolate

Depth (cm)		Atrazine				Alachlor			
		Control	Dry	Inter.	Wet	Control	Dry	Inter.	Wet
		Soil (µg/g)							
18.75-22.50	Mean†	0.015	0.077	0.113*	0.077	0.0005‡	0.033	0.070*	0.050
	SE §	(0.005)	(0.026)	(0.026)	(0.026)	(0.0005)	(0.025)	(0.025)	(0.025)
22.50-26.25	Mean	0.021	0.037	0.107*	0.090	0.0005‡	0.020	0.017	0.050**
	SE	(0.001)	(0.027)	(0.027)	(0.027)	(0.0005)	(0.0096)	(0.0096)	(0.0096)
26.25-30.00	Mean	0.0205	0.050	0.087**	0.093**	0.0005‡	0.017	0.013	0.053**
	SE	(0.0005)	(0.014)	(0.014)	(0.014)	(0.0005)	(0.012)	(0.012)	(0.012)
		Percolate (µg/mL)							
Perc.‖	Mean	0.0005‡	1.80***	1.29**	1.08**	0.0005‡	0.27**	0.20**	0.14*
	SE	(0.0005)	(0.25)	(0.25)	(0.25)	(0.0005)	(0.048)	(0.048)	(0.048)

*, **, *** For a given depth or percolate, the means are significantly greater than the control at P ≤ 0.05, ≤ 0.01, ≤ 0.001, respectively, by Dunnett's method.
† Mean herbicide concentration in soil from two (control) or three (dry, intermediate, wet) replications.
‡ Both control replicates had a value of zero but a negligible value was added to one replicate to permit the mixed model to converge.
§ The standard error of the control or the pooled standard error of the treatments.
‖ Flow-weighted average concentration, total transport in all cells divided by percolate volume. The percolate data was first presented by Shipitalo and Edwards (1996).

herbicide movement to 30 cm in the dry blocks even though the percolate concentrations were highest; whereas, the wet block soil samples showed some evidence of herbicide movement to 30 cm even though the percolate concentrations were lowest. In fact, there was no correlation of percolate concentration to soil concentration in the bottom-most soil layer (fig. 1). In addition, no correlation was observed between herbicide concentration in the bottom-most soil layer and herbicide mass transport in percolate (product of concentration and volume, data not shown) and the regressions were slightly negative. Although the correlations were not significant, these observations illustrate the futility of relating subsurface soil concentrations to herbicide concentration in percolate in a soil subject to macropore flow.

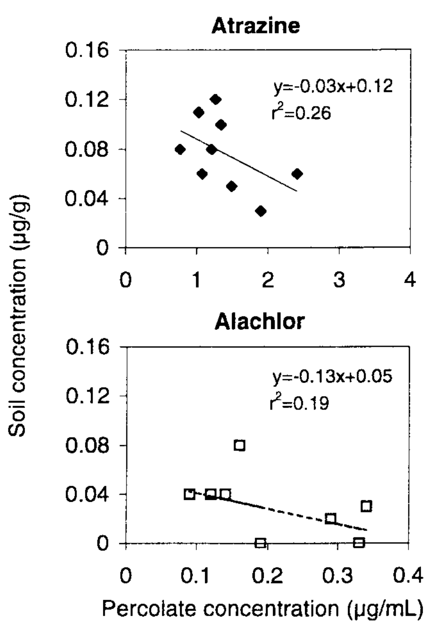

Figure 1–Herbicide concentration in bottom soil layer versus flow-weighted percolate concentration for each soil block except control. Note that two observations for alachlor were identical.

Herbicide concentrations in percolate from each of the moisture levels were significantly greater than the control, which had no herbicide added (table 2). The herbicide concentrations for the bottom three soil layers, however, were significantly greater than the control for only 7 of 18 treatment-depth means. Therefore, it could not be statistically established that the herbicide concentration for the bottom three soil layers were greater than background (control) for most of the treatment-depth means, due to the relatively low soil concentrations and the relatively high variability. This is further evidence that soil samples were a poor indicator of herbicide concentration in percolate.

Significant inverse relationships between natural log of relative herbicide concentration (concentration at a given time divided by average concentration) and natural log of time were noted for all water content levels (fig. 2). Therefore, the first water moving through the soil had the highest herbicide concentration. Steenhuis et al. (1994) also observed that herbicide concentrations decrease with cumulative outflow from macropores. This is further support that soil samples taken after rainfall may be a poor indicator of herbicide transport. If the herbicide concentrations in subsurface soil water are highest at the beginning of the event and lowest at the end of the event, relating herbicide concentration in the soil to herbicide transport in percolate is difficult. It cannot be argued that the main solute front had moved below 30 cm because

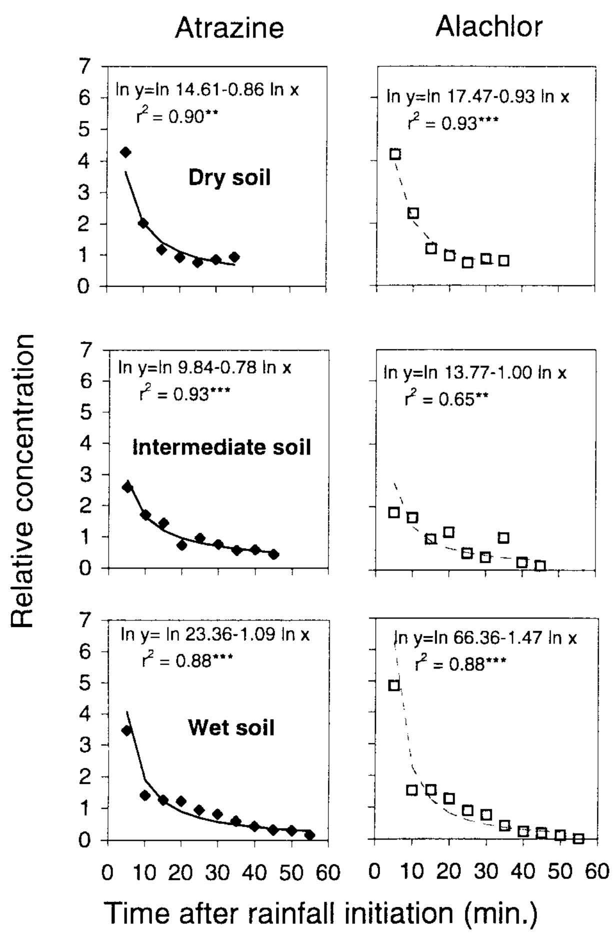

Figure 2–Relationship of relative herbicide concentration in percolate to minutes after rainfall. The symbols ** and * indicated significance at the 0.01 or 0.001 level, respectively.**

< 10% of the applied atrazine and < 1% of the applied alachlor leached out of the soil blocks. This also calls into question the suitability of suction (porous cup) lysimeter samples taken after a percolate event for assessing herbicide movement resulting from the event.

MODELING

The observed and GLEAMS-predicted herbicide distributions in soil are presented in figure 3. Calibration based on the surface soil herbicide concentration resulted in under prediction of herbicide concentration for the bottom soil depths (layers 3 and 4) for each herbicide-moisture combination, indicating that the calibrated K_{oc} may be too high. On the other hand, calibration based on the soil herbicide concentration in the bottom soil layer resulted in under prediction of surface soil concentrations (layer 1) and over prediction in the middle soil (layers 2 and 3) in each case, indicating that the calibrated K_{oc} may be too low.

Depending upon the objectives of the modeler, either calibration scenario could be considered acceptable when only soil samples are used to assess the model (considering

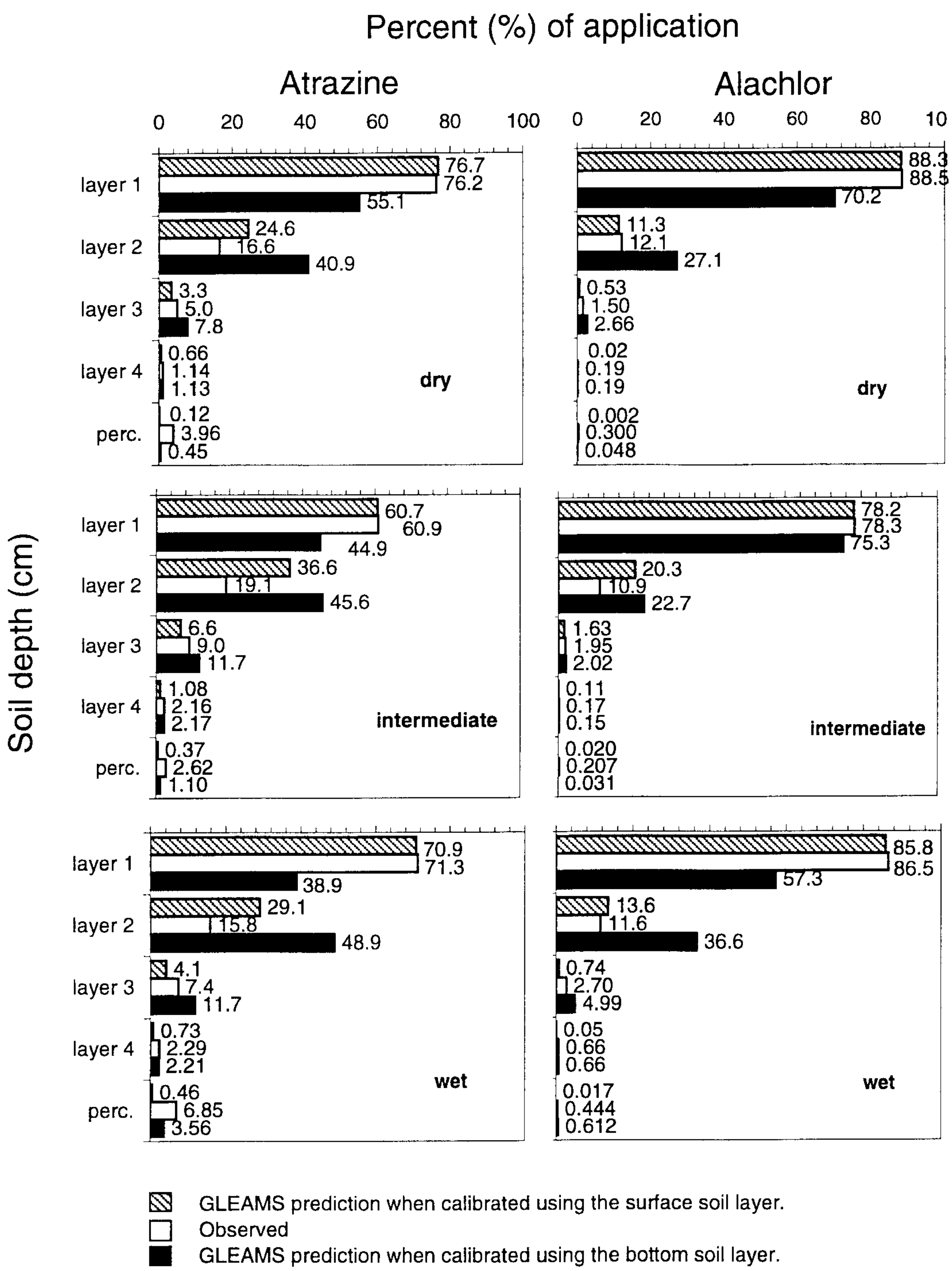

Figure 3–Observed chemical distribution in soil versus GLEAMS predicted chemical distribution. The observed distribution is the average of three replicates.

the distribution shown in fig. 3). For most modeling scenarios, it is likely that the calibrated K_{oc} would result in a distribution between the two extremes shown figure 3, and probably closer to the surface calibration scenario. The percolate concentrations were underpredicted by a factor > 7 (range of 7.5 to 122.7) for all herbicide-moisture combinations when the observed and predicted surface soil herbicide concentrations were calibrated to be nearly equal (table 3). Herbicide concentrations in the percolate were underpredicted by GLEAMS by a factor ≥ 6 for three of six herbicide-moisture combinations even though the observed and predicted bottom layer (26.25 to 30 cm) soil herbicide concentrations were calibrated to be nearly equal (table 3). This indicates that extreme caution should be exercised when a contaminant transport model is evaluated using soil cores when significant macropore flow might occur.

The percolate concentrations were underpredicted to a greater degree for the dry or intermediate soil water conditions (bottom layer calibration) where macropore flow was more prevalent compared to the wet soil. GLEAMS accurately simulated both alachlor and atrazine percolate concentration for wet soil conditions (bottom layer calibration), indicating that antecedent water content can affect model accuracy.

The modeling provides evidence that soil samples can be a poor method to assess herbicide mass transport in percolate. Table 3 shows that the herbicide concentrations in the percolate were often substantially underpredicted. But both the predicted percolate volume and the predicted herbicide soil concentrations for the bottom soil layer were nearly equal to the observed values. Therefore, herbicide mass transport in percolate computed using a model similar to GLEAMS with calibrated herbicide concentrations in soil and calibrated percolate volume may be inaccurate when macropores are active. Performing a mass balance without the aid of a computer model to estimate herbicide mass transport beyond a certain soil depth (30 cm in our case) is difficult with the uncertainty in herbicide half life in soil, soil bulk density, herbicide analysis in soil, herbicide application rate (drift and fast dissipation are sometimes a problem), and realizing that even a small percentage of herbicide loss in percolate (less than 1%) can lead to excessive concentrations in groundwater.

Table 3. GLEAMS predicted and observed herbicide concentrations in soil and in percolate

	Atrazine			Alachlor		
	Dry	Inter.	Wet	Dry	Inter.	Wet
Observed Data						
Bottom soil concentration (µg/g)*	0.050	0.087	0.093	0.017	0.013	0.053
Percolate concentration (µg/mL)†	1.80	1.29	1.08	0.27	0.20	0.14
Chemical in block (kg/ha) ‡	2.32	2.11	2.33	4.62	4.12	4.59
GLEAMS Predictions with Layer 1 Soil Concentration Calibrated (≈0 to 3.75 cm)						
Layer 4 soil concentration (µg/g)*	0.025	0.043	0.0724	0.002	0.009	0.004
Percolate concentration (µg/mL)	0.057	0.172	0.030	0.002	0.019	0.005
Ratio§	31.6	7.5	36.4	122.7	10.5	25.5
GLEAMS Predictions with Layer 4 Soil Concentration Calibrated (≈26.25 to 30 cm)						
Layer 4 soil concentration (µg/g)*	0.049	0.087	0.090	0.016	0.012	0.053
Percolate concentration (µg/mL)	0.210	0.516	0.564	0.045	0.029	0.194
Ratio§	8.6	2.5	1.9	6.0	6.9	0.7

* The observed (average of the three replicates) or predicted soil herbicide concentration at the lower soil layer (≈26.25 to 30 cm).
† The observed percolate concentration was first presented by Shipitalo and Edwards (1996).
‡ The total chemical recovered from blocks. Includes chemical in soil, percolate, and background.
§ Observed (flow-weighted) concentration in percolate divided by predicted concentration.

Table 4. Sensitivity analysis for the dry soil blocks

	Porosity Adjustment*		Field Capacity Adjustment †		O.M. Adjustment ‡		FC and Porosity Gradient §	
	Atrazine	Alachlor	Atrazine	Alachlor	Atrazine	Alachlor	Atrazine	Alachlor
Surface Soil Herbicide Concentration Calibrated (0-4.05 cm)								
K_{oc}	37	61	41	77	44	80	35	60
Ratio‖	24.2	32.9	29.2	122.7	30.0	71.1	25.0	67.5
Bottom Soil Herbicide Concentration Calibrated (26.65-30.0 cm)								
K_{oc}	22	39	19	33	25	43	14	28
Ratio‖	9.3	6.9	8.1	5.6	10.1	7.3	5.6	4.8

* The porosity was increased from 0.42 to 0.46. All other GLEAMS input except K_{oc} were maintained at table 1 values.
† The field capacity was increased from 0.33 to 0.40 and the initial water content (BST) was increased from 0.6 to 0.7. All other GLEAMS input except K_{oc} were maintained at table 1 values.
‡ The organic matter in layer 2 was decreased from 4.5 to 2.5. All other GLEAMS input except K_{oc} were maintained at table 1 values.
§ The porosity for layers 1-4 was 0.44, 0.43, 0.41, and 0.40, respectively. The field capacity for layers 1-4 was 0.40, 0.27, 0.20, and 0.22, respectively. It is recognized that the field capacity gradient is possibly unrealistic; this scenario was inserted to equate observed and predicted post-rain water content.
‖ Observed (flow-weighted) concentration in percolate divided by predicted concentration.

Sensitivity Analysis

The parameter input for GLEAMS was somewhat simplistic so a sensitivity analysis was performed for the dry soil blocks. The main goal of this analysis was to determine the effect of different input scenarios on the ratio of observed to predicted percolate concentration, therefore we wanted to maintain equivalent predicted and observed soil concentration (either upper or lower soil layer). To accomplish this, the analysis included adjusting the parameter in question (porosity, field capacity, organic matter, or field capacity and porosity gradient), recalibrating the percolate volume by adjusting the initial water content (BST), then recalibrating the upper soil layer (0 to 4.05 cm) or lower soil layer (26.65 to 30.0 cm) herbicide concentration by adjusting the partition coefficient. Although adjusting the input parameters affected the ratio of observed to predicted percolate concentration for the dry soil condition (table 4), our conclusions remain essentially unchanged: GLEAMS substantially underpredicted percolate concentration even under the conservative case (for our objectives) of calibrating the bottom soil concentration.

Conclusion

In conclusion, the soil sampling strategy used in this study was a poor indicator of subsurface herbicide movement in percolate, and was a poor method to assess a contaminant transport model. Areas of further research would be to determine: (1) if tension (porous cup) lysimeter samples are representative of herbicide concentrations in percolate; (2) if soil samples are suitable for assessment of models with a macropore component (e.g., RZWQM); and (3) if similar results would be observed with different soil types, sample size, sampling strategies, and soil block depths.

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